

EPR OF CH₃ RADICALS IN SiO₂ CLATHRATE

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EPR lineshape simulations of CH₃/SiO₂ clathrates reveal the motional conditions of the CH₃ radical up to the unusual regime of its stability, the high temperature diffusional regime. This was obvious by the isotropic magnetic interaction at the highest experimental temperatures over 140 K. Special motional and thermodynamics conditions for methyl radical may however prevail for the CH₃/SiO₂ clathrates system due to the limited space of the host voids, compared to solid gas isolation. The lowest temperature in the experiment was 4.1 K, while the highest one was 300 K. The EPR parameters of the radical revealed non-monotonic temperature dependence. The extremely wide temperature range of the radical stability may be attributed to the solidity of the clathrate voids and the small diameter of their channels that do not allow molecular collisions between the radical species. At the lowest sample temperatures, a portion of the radicals stopped to rotate thus indicating their attachment to specific matrix sites with large radical-host interaction. The unusual increase of the width of the CH₃/SiO₂ clathrate spectra with the temperature at high sample temperatures indicates resemblance to the spin-rotation interaction relaxation mechanism known only in the case of small species in non-viscous fluids, and is contrasted to the normal diffusional decrease of the width in the CH₃ hosted in a series of solid. The effect was explained by adopting extremely frequent radical collisions with the clathrate void walls leading to repeated angular momentum alterations, a kind of “reorientation”.^a

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